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## **STRAINED RING ENERGETIC BINDERS**

### **Final Report**

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The use of thermoplastic elastomers (TPEs) containing strained hydrocarbon rings as energetic propellant binders is an attractive approach to increasing the performance of highly oxidized propellant formulations which currently use HTPB as a binder. The recently reported strained-ring elastomeric polymer polybenzvalene (PBV), produced by ring-opening metathesis polymerization (ROMP), is an example of a strained ring polymer. However, PBV is thermally unstable ( $T_{onset} = 77^\circ\text{C}$ ,  $T_{max} = 137^\circ\text{C}$ ) and deflagrates under severe mechanical stretching.

In this program several areas were investigated. First, studies to attempt the thermal stabilization of PBV were undertaken. One approach was the partial reduction of the double bonds present in PBV which gave only small increases in thermal stability ( $\Delta T_{max} = 9^\circ\text{C}$ ). The second approach was the addition of radical traps to PBV which, again, gave only small increases in thermal stability ( $\Delta T_{max} = 8^\circ\text{C}$ ). The second area investigated a different strained ring polymer, polyhomobenzvalene (PHBV). PHBV was not found to have the mechanical instability problems of PBV, but was still thermally unstable ( $T_{onset} = 66^\circ\text{C}$ ,  $T_{max} = 109^\circ\text{C}$ ). The last area studied was the application of acyclic olefins as chain-transfer agents during polymer formation which produced difunctional hydroxytelechelic polymers of cyclooctene and cyclooctadiene (as model systems) with good control of molecular weight.

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## SUMMARY

The use of thermoplastic elastomers (TPEs) containing strained hydrocarbon rings as energetic propellant binders is an attractive approach to increasing the performance of highly oxidized propellant formulations which currently use HTPB as a binder. The recently reported strained-ring elastomeric polymer polybenzvalene (PBV), containing alternating bicyclobutane and ethylene units, is an example of a strained ring polymer. This energetic polymer is formed by the ring-opening metathesis polymerization (ROMP) of benzvalene, utilizing a tungsten-based catalyst. In theoretical calculations, PBV shows a significant gain in  $I_{vac}$  over R-45M for highly oxidized formulations.

However, PBV is thermally unstable ( $T_{onset} = 77^\circ\text{C}$ ,  $T_{max} = 137^\circ\text{C}$ ) and deflagrates under severe mechanical stretching. The instability of PBV is believed to proceed by a radical-initiated process which requires the double bonds present in the polymer. Reduction of the double bonds to give a saturated polymer should stabilize PBV by eliminating this decomposition pathway. Additionally, treatment with compounds which might trap the radical intermediates involved in the proposed decomposition process would also achieve the same result.

In this report are first outlined studies which attempted to increase the stability of PBV. One approach was the reduction of the double bonds present in PBV by several different hydrogenation methods, including *p*-tosylhydrazine, hydrazine hydrate/ $\text{K}_3\text{Fe}(\text{CN})_6$ , and Wilkinson's catalyst/hydrogen. Unfortunately, hydrogenation only proceeded to a small degree with these methods and only limited increases in thermal stability ( $\Delta T_{max} = 9^\circ\text{C}$ ) were observed. The second approach was the addition of radical traps to PBV. These compounds included butylated hydroxytoluene (BHT) and the similar antioxidant AO 2246. Again, only a small increase in thermal stability ( $\Delta T_{max} = 8^\circ\text{C}$ ) was obtained. All of the studies involving PBV were hindered by the insolubility of the polymer once it was precipitated from solution.

Several other strained ring polymers similar to PBV are known. The investigation of one of these polymers, polyhomobenzvalene (PHBV), is also described in this report. PHBV contains alternating bicyclopentane and ethylene units. Calculations have demonstrated about 80% of the impulse gain compared with PBV in several highly oxidized formulations. A soluble form of PHBV was finally produced using a newly developed ruthenium catalyst. The polymer was characterized by NMR and GPC. PHBV was found not have the mechanical instability problems of PBV, but still was not very thermally stable ( $T_{onset} = 66^\circ\text{C}$ ,  $T_{max} = 109^\circ\text{C}$ ).

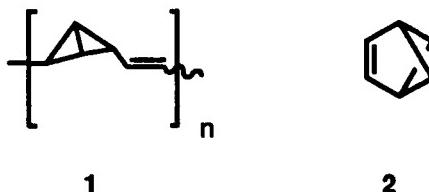
The last area studied and reported on is a potential end group functionalization method for strained ring polymers produced by ROMP. This method allows for the utilization of strained ring polymers as building blocks for TPE propellant binders. Application of acyclic olefins as chain-transfer agents during polymer formation, previously demonstrated in other ROMP systems, produced difunctional hydroxytelechelic polymers of cyclooctene and cyclooctadiene (as model systems) with good control of molecular weight.

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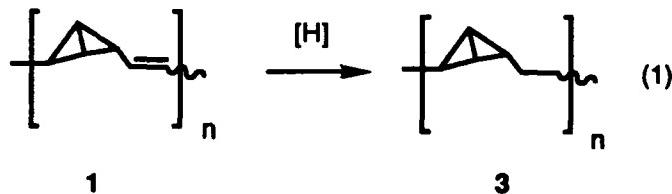
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## INTRODUCTION

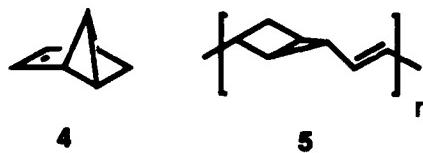
The use of thermoplastic elastomers (TPEs) containing strained hydrocarbon rings as energetic propellant binders is an attractive approach to increasing the performance of highly oxidized propellant formulations which currently use HTPB as a binder. The recently reported strained-ring elastomeric polymer polybenzvalene (PBV) (1) (11 kcal of ring strain/carbon) containing alternating bicyclobutane and ethylene units is an example of a strained ring polymer.<sup>1</sup> This energetic polymer is formed by the ring-opening olefin metathesis polymerization (ROMP<sup>2</sup>) of benzvalene (2) utilizing a tungsten-based catalyst.<sup>3</sup> In theoretical calculations using a measured heat of formation, PBV shows a significant gain in  $I_{vac}$  over R-45M for highly oxidized formulations.



However, PBV is unstable towards severe mechanical stretching and deflagrates under these conditions. Therefore, the employment of PBV in a TPE propellant binder requires the stabilization of this material to withstand the stresses encountered during propellant formulation, mixing, and casting. The stress-produced decomposition of PBV is believed to proceed by a radical-initiated process which requires the participation of the carbon-carbon double bonds present in the polymer. Reduction of the double bonds to produce the saturated polymer 3 (eq 1) should stabilize PBV by eliminating the decomposition pathway and give a suitable elastomer for use as the soft block of a TPE propellant binder. Additionally, treatment with compounds which might trap the radical intermediates involved in the proposed decomposition process would also achieve the same result.



The monomer homobenzvalene (4)<sup>4</sup> and subsequent polymer polyhomobenzvalene (PHBV, 5)<sup>5</sup> are also known materials. Calculations have demonstrated about 80% of the impulse gain compared with PBV in several highly oxidized formulations. More importantly, PHBV does not demonstrate the instability which PBV has towards severe mechanical stretching.



Application of strained ring binders in propellants would be expected to increase the  $I_{vac}$  values of these propellants as compared to conventional hydrocarbon binders because of the additional energy content present from the strained rings (see above). To determine the expected gain in impulse, a series of calculations were performed with the calculated heats of formation. The highly oxidized formulation used consisted of 14% Be, 71% HAP, and 15% binder. The gain in performance for strained ring hydrocarbon binders is most dramatic for this proposed highly energetic system. The results from the calculations are given in Table 1 below.

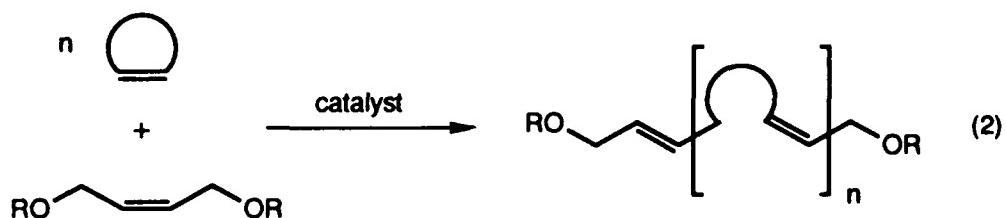
The calculated increase in  $I_{vac}$  obtained by substituting PBV for R-45M/IPDI is a significant amount (4.0 seconds). The hydrogenated version of PBV, binder 3, also shows the same increase in  $I_{vac}$  over R-45M. The identical values for 1 and 3 are actually due to the opposing influences of the greater hydrogen content of 3 ( $C_6H_8$  versus  $C_6H_6$ ) which is offset by the smaller heat of formation of 3. Without its strain energy, binder 3 shows a decrease of 0.8 seconds compared to R-45M, due to the lower amount of hydrogen present in binder 3. The last entry in Table 1 shows that the strained ring binder PHBV (5) calculates to give 80% of the increase in  $I_{vac}$  compared to 1 or 3.

**Table 1.** Calculated  $I_{vac}$  values for several binder systems.\*

entry	binder	$\Delta H_f$ (kcal/mol)	$I_{vac}$ (lb-sec/lb)	$\Delta I_{vac}$
#1	R-45M/IPDI	-12.0	355.4	—
#2	1	+56.2	359.4	4.0
#3	3	+50.0	359.4	4.0
#4	3 (no strain)	-9.30	354.6	-0.8
#5	5	+40.0	358.6	3.2

\* The formulation consisted of 14% Be, 71% HAP, and 15% binder. The R-45M/IPDI binder system consisted of 14% R-45M and 1% IPDI. The value of  $A_e/A_t$  is 50. The heats of formation ( $\Delta H_f$ ) were calculated using known methods.<sup>6</sup> The  $I_{vac}$  values were calculated using the NASA-Lewis program for theoretical rocket performance assuming equilibrium composition during expansion. The change in  $I_{vac}$  ( $\Delta I_{vac}$ ) is the  $I_{vac}$  value of the binder minus the  $I_{vac}$  value for R-45M/IPDI.

In order to utilize strained ring polymers as building blocks for TPE propellant binders, a facile method of linking the requisite hard and soft block polymers must be employed. One attractive method is the block linking of hydroxy-terminated polymers to give TPEs.<sup>7</sup> The hydroxytelechelic strained ring polymers required for this approach necessitate the development of an end group functionalization method to apply to these polymers. Application of acyclic olefins as chain-transfer agents during the polymerization, previously attempted in other ROMP systems,<sup>8</sup> would make this functionalization possible (eq 2).

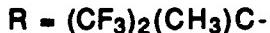
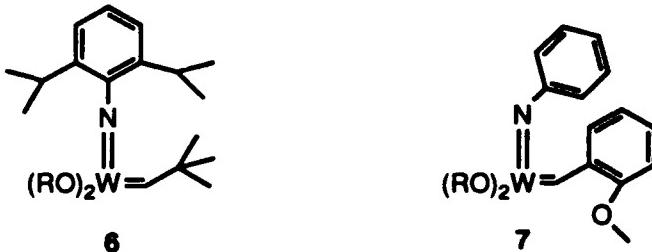


## RESULTS AND DISCUSSION

### Polybenzvalene(PBV)

The monomer benzvalene (**2**) was synthesized by a modified procedure from that given in the literature.<sup>9</sup> These modifications (given in the Experimental Section) allow for the one pot reaction to be completed in six hours or less, to give a 15-20% yield of the monomer in solution. The monomer solutions (20-30% by weight benzvalene diluted in a mixture of dichloromethane, benzene, and hexanes) were stored at -50°C due to the thermal instability of benzvalene. Care should be exercised during the preparation of benzvalene to prevent isolation of the neat material as it has been reported to be a contact explosive.

The polymerization of benzvalene in previous work was achieved using the tungsten catalyst **6**.<sup>1</sup> For the studies of this report the polymerization was achieved with the new tungsten catalyst **7**.<sup>10</sup> In a typical polymerization the catalyst was dissolved in toluene, the resulting solution cooled to 0°C, and the benzvalene solution added by syringe. The stirred mixture was then allowed to warm to room temperature. The polymerization was complete 0.5 hours after addition of the monomer, as determined by NMR analysis of a sample of the mixture. The catalyst was then quenched by the addition of dry, deoxygenated acetone. The PBV was isolated from the toluene solution by precipitation into methanol. PBV isolated by this method would not dissolve in any organic solvents, as was reported previously.<sup>1</sup> If polymerizations were allowed to proceed for several hours, the mixture would become much darker and polymer would precipitate from solution. The following stabilization studies discussed in this report utilized toluene solutions of freshly prepared PBV straight from the polymerization mixture.



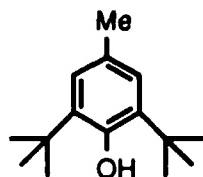
Initial work on the hydrogenation of PBV examined the heating of the polymer in xylenes in the presence of *p*-tosylhydrazine.<sup>11</sup> This method of reduction has also been utilized for several ROMP systems.<sup>12</sup> Unfortunately, the temperature of the reaction (100°C) caused crosslinking of PBV and its resultant precipitation from the reaction mixture. The precipitated polymer exhibited a slight decrease in stability compared to PBV as determined by DSC analysis (Table 2). This is probably due to the presence of unreacted *p*-tosylhydrazine trapped in the precipitated polymer sample. The second method attempted utilized the combination of hydrazine hydrate and potassium ferricyanide, a system known to reduce the double bond present

in benzvalene and leave the bicyclobutane portion intact.<sup>9</sup> Again, polymer precipitation, leading to crosslinking, was a problem. In this instance it was due to the very polar solvent combination required for the reaction. DSC analysis gave similar results to the *p*-tosylhydrazine treatment described above, probably for the same reason. The next method examined involved utilization of Wilkinson's catalyst,<sup>13</sup> Rh(PPh<sub>3</sub>)<sub>3</sub>Cl, and hydrogen. A slight uptake of hydrogen was noted over a four hour period, indicating partial hydrogenation of the PBV sample. DSC showed a slight increase in the temperature of the first exotherm. This result is encouraging as it indicates that partial reduction of the double bonds present in PBV leads to a perceptible stabilization of the polymer.

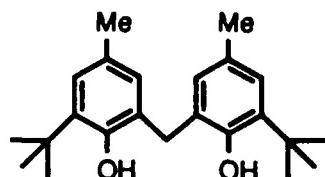
**Table 2.** DSC Results From Hydrogenation Studies of PBV

method	1st exotherm	2nd exotherm
	T(max)(°C)	T(max)(°C)
original sample of PBV	150	300
<i>p</i> -tosylhydrazine	142	—
hydrazine hydrate/K <sub>3</sub> Fe(CN) <sub>6</sub>	136	213
Wilkinson's catalyst/hydrogen	159	297

The next set of experiments involved the addition of the antioxidants BHT and AO 2246 to samples of freshly synthesized PBV. The stabilization of ROMP polymers towards radical-initiated crosslinking was previously observed using this method.<sup>14</sup> The results from these studies are presented in Tables 3 and 4. The first point to note is that the T<sub>max</sub> value for untreated PBV decreased from 150°C in earlier hydrogenation studies to 137°C in these studies. This difference may be attributable to using unsealed DSC pans in earlier studies compared to sealed DSC pans in later studies. In comparing the relative values in Table 3 and 4, there appears to be a modest increase in the thermal stability of the PBV samples in the presence of either radical trap. A gradual increase in stability was observed at the higher concentrations of stabilizer. These antioxidants do not appear viable for stabilizing PBV (but other radical traps may be more effective).



BHT



AO 2246

**Table 3.** Stabilization of PBV by the Addition of BHT

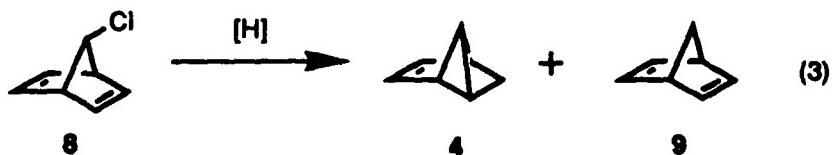
1st exotherm	
% BHT (by weight)	T(max)(°C)
0	137
3	140
6	140
11	145

**Table 4.** Stabilization of PBV by the Addition of AO 2246

1st exotherm	
% AO 2246 (by weight)	T(max)(°C)
0	137
3	141
18	142

#### Polyhomobenzvalene(PBV)

The monomer homobenzvalene (**4**) and subsequent polymer polyhomobenzvalene (**PHBV**) (**5**) are known materials. The established synthesis of **4** involves the reaction of 7-chloronorbornadiene<sup>15,16</sup> (**8**) with lithium aluminum hydride (LAH) in diethyl ether to give a 1:1 ratio of **4** and the side product norbornadiene (**9**)(eq 3).<sup>4</sup> Polymerization of this mixture in benzene with the catalyst **6** gave an insoluble polymer.<sup>5</sup> The polymer precipitation may have resulted from the interaction of the Lewis acidic tungsten catalyst and the strained hydrocarbon rings present in the polymer. In order to utilize PHBV in the current studies a better synthesis of the monomer was required and also a ROMP catalyst was needed that would not decompose the polymer during its preparation.



A set of experiments was performed to improve the synthesis of **4**. A summary of the results are presented in Table 5. The yields were determined by GC analysis of the crude product obtained. Changing the reducing reagent from LAH to NaBH<sub>4</sub> lead to a significant lowering in the quantity of norbornadiene (**9**) produced as a side product. The reaction gave the best yield of **4** (78%) when run in methanol overnight with NaOH also present in the reaction mixture. The solution of **4** in methanol produced requires the use of a ROMP catalyst which is

stable in methanol (see below). A solution of 4 in benzene could also be formed in lower yield (58%) , employing a phase transfer catalyst in a benzene/water solvent mixture of 8, NaOH, and NaBH<sub>4</sub>. This benzene solution, once dried over calcium hydride, is amenable to polymerization by a variety of ROMP catalysts.

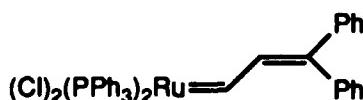
**Table 5. Improving the Synthesis of Homobenzvalene (4)**

solvent	base	reagent	time	% 4	% 8	% 9
ether	—	LAH	3h	50	—	50
MeOH	NaOH	NaBH <sub>4</sub>	18h	78	—	5
MeOH (dry)	NaOH	NaBH <sub>4</sub>	18h	41	30	2
MeOH (dry)	NaOMe	NaBH <sub>4</sub>	3h	18	—	—
MeOH/H <sub>2</sub> O	NaOH	NaBH <sub>4</sub>	4h	28	—	2
THF (dry)	—	NaBH <sub>4</sub>	3h	—	100	—
THF/H <sub>2</sub> O	NaOH	NaBH <sub>4</sub>	3h	32	23	8
Ph/H <sub>2</sub> O*	NaOH	NaBH <sub>4</sub>	18h	58	5	20

\*employed benzyltrimethylammonium chloride as a phase transfer catalyst

The first polymerization of 4, in methanol, was attempted with the catalyst Ru(H<sub>2</sub>O)<sub>6</sub>(tosylate)<sub>2</sub>. This catalyst has been show to be an effective ROMP catalyst in the presence of alcohols and even water.<sup>17</sup> Unfortunately, the polymer produced was insoluble and could not be characterized. The polymerization was next attempted employing a benzene solution of 4 with the tungsten catalyst 7. Again, the polymer formed was insoluble and precipitated from the polymerization mixture after 0.5 hours.

The development of the new ruthenium ROMP catalyst 10<sup>18</sup> prompted further efforts to produce a soluble form of PHBV. To a mixture of the partially soluble 10 in toluene at room temperature was added a toluene solution of 50 equivalents of 4 by syringe. After a few minutes the dark green mixture (unreacted catalyst) turned to a clear orange-brown color. A sample of the mixture was examined by proton NMR and signals corresponding to 4 decreased in intensity and new signals corresponding to 5 appeared. After 2.0 hours the polymerization was complete by proton NMR. Little, if any, of the norbornadiene (9) present was consumed during the



10

polymerization. The polymer was isolated by precipitation into methanol. In contrast to previous attempts to prepare PHBV, the isolated polymer could be redissolved in benzene, dichloromethane, and THF. This permitted characterization by GPC, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. GPC gave an M<sub>n</sub> value of 5,400 and M<sub>w</sub> value of 20,400 versus polystyrene standards. The

monomer/catalyst ratio employed would have predicted a  $M_n$  value of 4,600.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PHBV prepared are presented in Figures 1 and 2. Due to the presence of a variety of microstructures possible with the unsymmetrical repeat unit of PHBV, no definite assignments could be made in the NMR spectra. However, in the  $^1\text{H}$  NMR spectrum, comparison of the integration of the olefinic region (two protons) and aliphatic region (six protons) is in agreement with the structure of PHBV. Additionally, one of the methine aliphatic protons appears as a group of peaks at 3-4 ppm while another methine proton appears as a multiplet at 2.3 ppm. In the  $^{13}\text{C}$  NMR spectrum, a multitude of peaks corresponding to olefinic carbons are present at 120-133 ppm while peaks from 12-46 ppm can be assigned to aliphatic carbons.

A second sample of PHBV was prepared employing 99 equivalents of the monomer. The isolated polymer was not as soluble as the first sample and GPC analysis in THF was not feasible. However, in the  $^1\text{H}$  NMR spectrum the integration of the the protons of diphenylethylene end group from the catalyst compared to the monomer protons gave a calculated molecular weight of 12,700. The monomer/catalyst ratio employed would have predicted a molecular weight of 9,100. The second sample of PHBV was also analyzed by DSC to determine its thermal stability. Surprisingly, the polymer was found to be less stable than PBV. The measured onset of decomposition (as evidenced by an exotherm) was at 66°C with the maximum of the exotherm occurring at 109°C.

Therefore, PHBV is appears to be less thermally stable than PBV. However, it does not exhibit the impact and friction sensitivity observed previously with PBV. Finally, the solubility of PHBV produced with catalyst 10 make PHBV amenable to possible derivatization methods which might afford greater thermal stability.

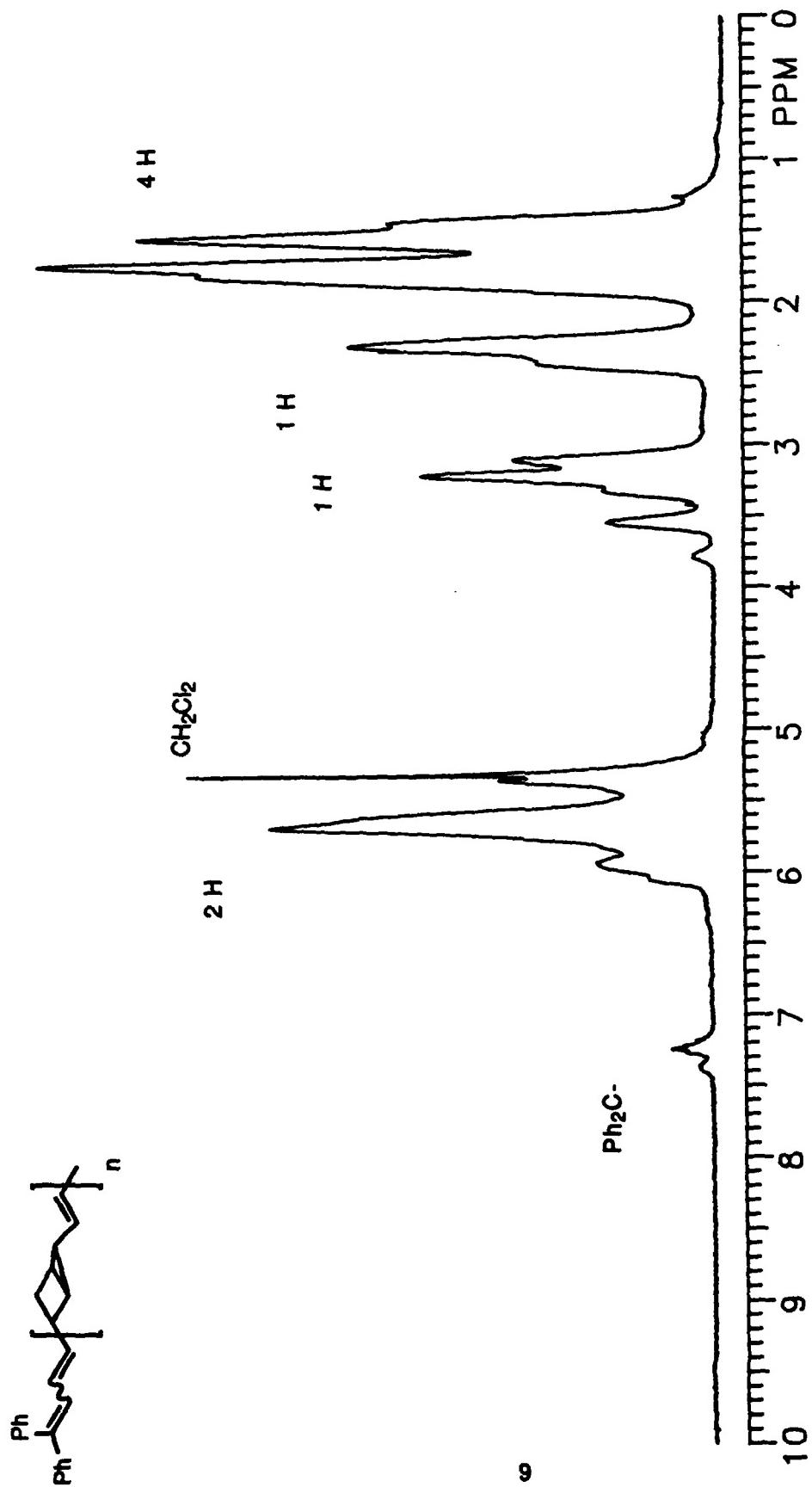


Figure 1. 300 MHz  $^1\text{H}$  NMR Spectrum in  $\text{CD}_2\text{Cl}_2$  of Polyhomobenzvalene

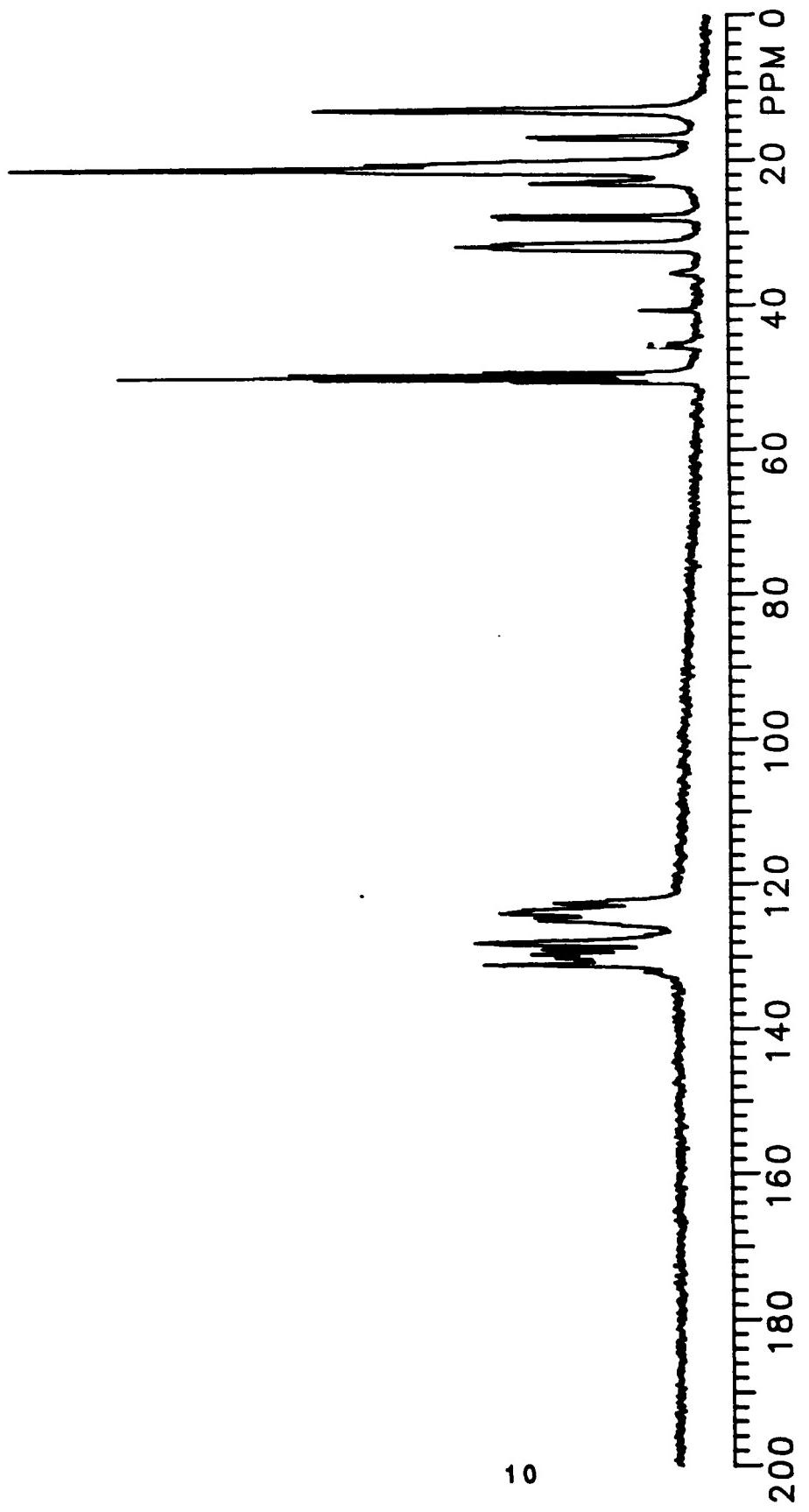
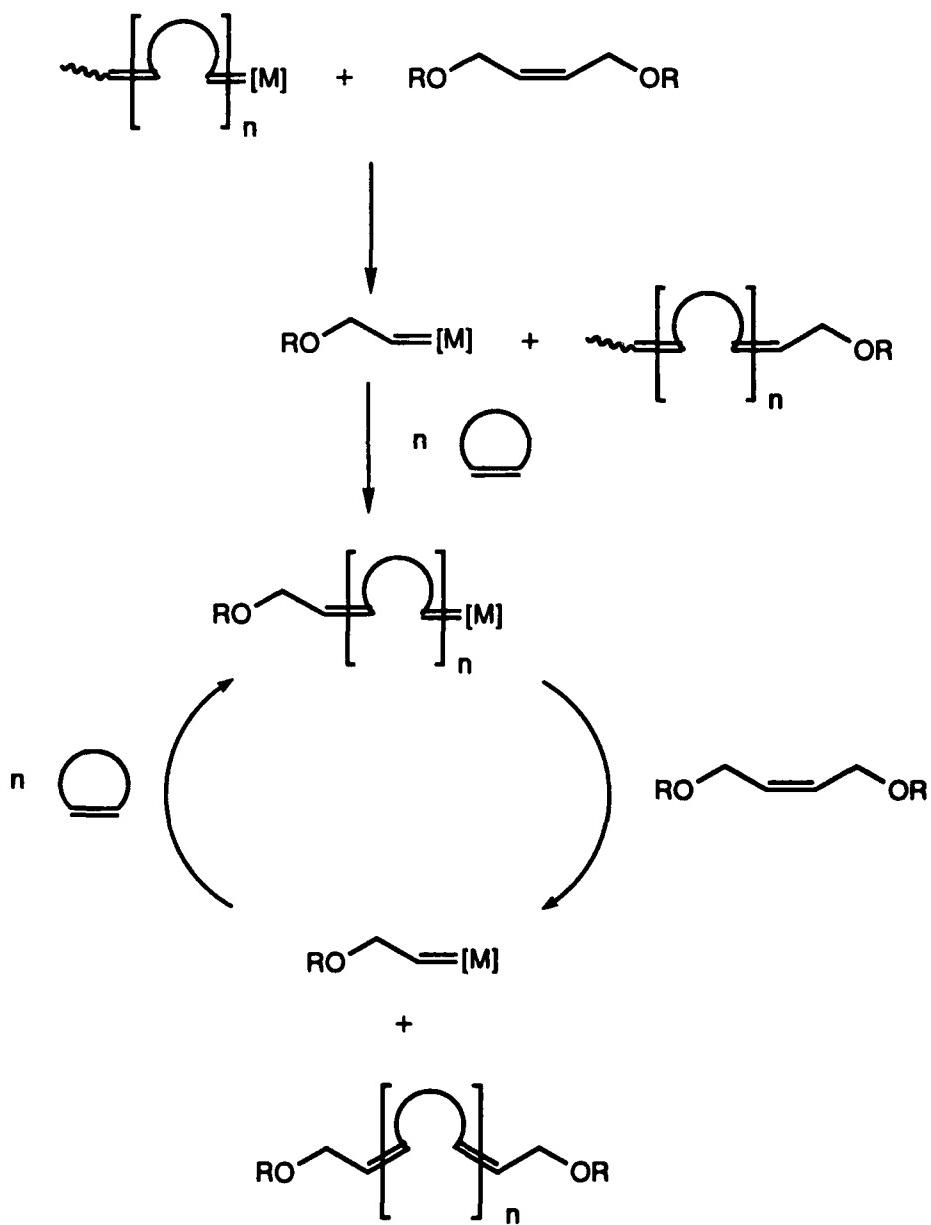


Figure 2. 75.4 MHz  $^{13}\text{C}$  NMR Spectrum In  $\text{CD}_2\text{Cl}_2$  of Polyhomobenzvalene

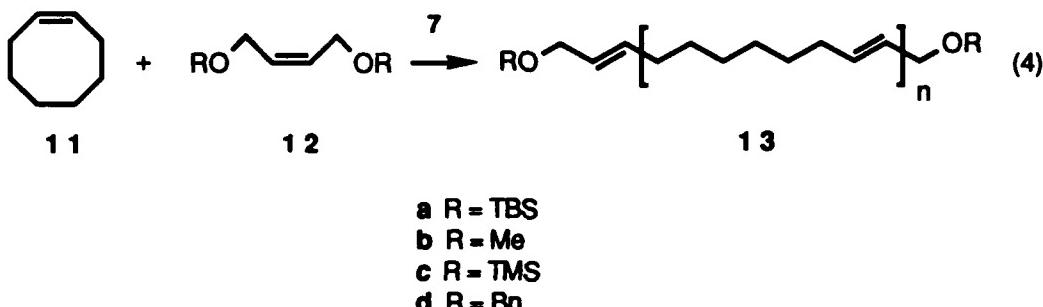
### Chain-Transfer Studies

In support of the work to synthesize stable, strained ring TPE propellant binders, studies were also performed to functionalize the end groups of ROMP polymers by chain transfer. The development of this technique would allow for the chemical linking of the strained ring hard and soft blocks of the TPEs. The mechanism by which the chain transfer agent gives the desired end-functionalized polymers is presented in Figure 3.

**Figure 3.** Mechanism of End-Group Functionalization by Chain-Transfer during ROMP



Initial model studies employed the monomer cyclooctene (11), the chain-transfer agents 12, and the tungsten catalyst 7<sup>10</sup> to give the polyoctenamer 13 (eq 4). The chain-transfer agents 12 were synthesized from *cis*-1,4-butenediol and the appropriate electrophile.



For the chain-transfer agents 12a (R = *tert*-butyldimethylsilyl (TBS)) and 12b (R = methyl (Me)), a series of polymers were made with different ratios of 12 to 11. The results from these polymerizations are presented in Tables 6 and 7, respectively. The data obtained indicates that the molecular weight of the polyoctenamer produced can be controlled by the ratio of chain-transfer agent to monomer. One significant advantage of using this method to produce ROMP polymers is the low amount of catalyst required to carry out the polymerizations.

**Table 6.** Chain-Transfer Polymerization of 11 Utilizing 12a

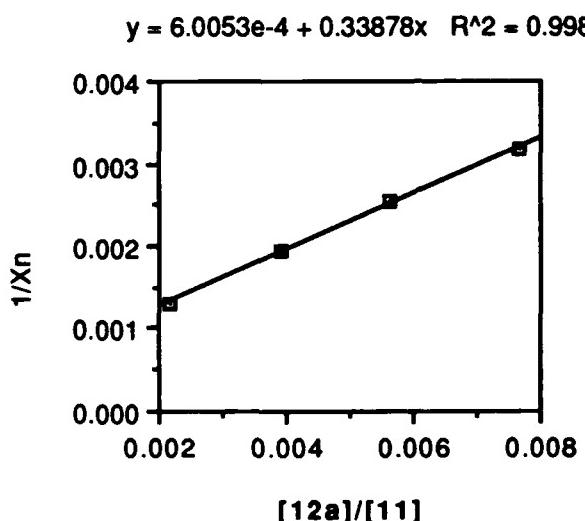
run	[12a]/[11]	[11]/[7]	Mn	Mw	PDI
#1	0.00215	559	84,400	140,300	1.7
#2	0.00393	672	56,500	103,400	1.8
#3	0.00562	579	43,200	81,100	1.9
#4	0.00765	618	34,800	67,100	1.9

**Table 7.** Chain-Transfer Polymerization of 11 Utilizing 12b

run	[12b]/[11]	[11]/[7]	Mn	Mw	PDI
#1	0	675	70,800	185,000	2.6
#2	0.00216	624	30,900	82,400	2.7
#3	0.00497	625	27,100	57,000	2.1
#4	0.00657	622	13,700	31,700	2.3

To test if the polymerizations are proceeding by the mechanism proposed in Figure 3, one can check to see if there is an inverse proportionality between the molecular weight of the polymer produced and the ratio of chain transfer agent to monomer employed. The proposed mechanism would predict this inverse relationship. The corresponding plot was made using the data from Table 6 and is shown in Figure 4. A good correlation is indeed observed, indicating chain transfer is probably occurring by the proposed mechanism.

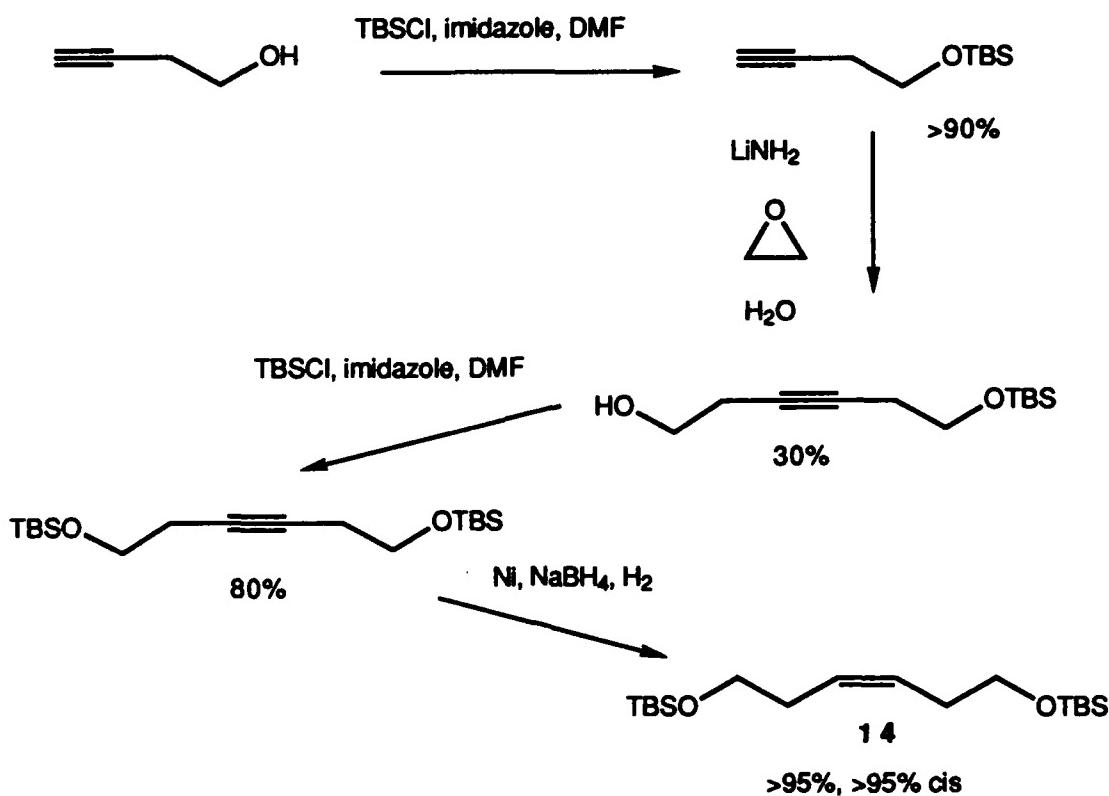
**Figure 4.** Demonstration of Chain Transfer



One problem encountered during the use of the chain-transfer agents 12 was that at higher ratios of 12 to 11 (higher concentrations of 12), yields of polymer as low as 40% were obtained (see Appendix A). This was probably a result of catalyst decomposition by the interaction of the oxygen atoms of 12 with the electrophilic tungsten present in the catalyst 7. Addition of extra methylene groups between the olefin bond and the oxygen would be expected to reduce the possibility of this decomposition pathway. Therefore, a new chain-transfer agent, 14, with an extra methylene group between the oxygen atom and olefin bond was synthesized (Figure 5) and employed as above to polymerize cyclooctadiene. The resulting polymerizations gave higher yields (83-94%) of polyoctadienamer, even at higher ratios of 14 to 11 (see Appendix B).

The polymers produced using the chain-transfer agents 12a,c and 14 can be easily deprotected with tetra-n-butylammonium fluoride at room temperature to give the corresponding hydroxy-terminated polymers. In the case of the deprotected polyoctadienamers, the polymers obtained are actually high cis content, hydroxy-terminated polybutadienes containing no vinyl groups.

**Figure 5.** Synthesis of Chain-Transfer Agent 14



## CONCLUSIONS

Current evaluation of the strained ring polymers, polybenzvalene (PBV) and polyhomobenzvalene (PHBV), would have to conclude that these materials do not have the thermal stability required to be considered viable solid propellant binders. PBV is thermally unstable ( $T_{onset} = 77^\circ\text{C}$ ,  $T_{max} = 137^\circ\text{C}$ ) and deflagrates under severe mechanical stretching. Studies which attempted to increase the stability of PBV were of limited success. Partial hydrogenation of PBV gives a small increase in thermal stability ( $\Delta T_{max} = 9^\circ\text{C}$ ). The addition of radical traps to PBV also produces only a small increase in thermal stability ( $\Delta T_{max} = 8^\circ\text{C}$ ). All of the studies involving PBV were hindered by the insolubility of the polymer once it was precipitated from solution.

A soluble form of the strained ring polymer PHBV was produced using a newly developed ruthenium catalyst. The polymer was characterized by NMR and GPC. PHBV was found not have the mechanical instability problems of PBV, but still was not very thermally stable ( $T_{onset} = 66^\circ\text{C}$ ,  $T_{max} = 109^\circ\text{C}$ ).

Application of acyclic olefins as chain-transfer agents during ROMP produces, after deprotection of the alcohol end-groups, difunctional hydroxytelechelic polymers of cyclooctene and cyclooctadiene with good control of molecular weight. This method allows for the end group functionalization of ROMP-derived polymers. These functionalized polymers could be chemically-cured or utilized as soft and hard blocks in the block-linking method of synthesizing TPEs.

## EXPERIMENTAL PROCEDURES

**General Methods.** All work involving air- and/or moisture-sensitive compounds was performed using standard high-vacuum or Schlenk techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4A molecular sieves and a Vacuum Atmospheres drybox under nitrogen.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Associates XL-300 (300 MHz  $^1\text{H}$ , 75.4 MHz  $^{13}\text{C}$ ). Polymerizations were carried out in glass tubes equipped with a stir bar, Teflon valve, and a female 14/20 joint for attachment to a dual manifold high vacuum line.

**Materials.** The catalysts 6, 7, and 10 were prepared as previously described.<sup>3,10,18</sup> The dichloromethane used for benzvalene synthesis was dried over  $\text{P}_2\text{O}_5$ , degassed by three freeze-pump-thaw cycles, and vacuum-transferred into a solvent flask equipped with a Teflon valve. The toluene,  $d_6$ -benzene, and xylenes used in polymerizations were purified by distillation from sodium benzophenone ketyl into solvent flasks equipped with Teflon valves. Acetone used to quench polymerizations was dried over 4 Å molecular sieves, vacuum-transferred to a dry glass tube, freeze-pump-thaw degassed and stored in a glass tube with a Teflon valve.

**Benzvalene.** Typical yields for this reaction were 15-20%. An optimized procedure is given below. **CAUTION!!** Care should be taken during the preparation of benzvalene as the neat material has been reported to be a contact explosive.

A two liter flask was charged with lithium cyclopentadienide (52.2 g, 730 mmol, 1.0 equiv) and flushed with argon. An overhead stirrer, addition funnel, and dry ice condenser were attached to the flask along with gas inlet and exit ports. The flask was cooled to -78°C in an isopropanol/dry ice bath and 800 grams of dimethyl ether was condensed into the flask after passage through a tower of activated 4 Å sieves. The flask was then warmed to -35°C. To the stirred mixture was added dry, deoxygenated dichloromethane (68 mL, 1,065 mmol, 1.46 equivs) by syringe with no noticeable exotherm. The addition funnel was then charged with 86 mL of 3.1 M sec-butyl lithium (783 mmols, 1.07 equivs) in hexanes and this material was added dropwise over a one hour period. The addition of each drop produced a hissing sound and constant cooling was required to maintain the flask temperature at -35°C.

After the addition was complete, a series of three traps were connected to the gas exit port of the flask and each trap was cooled to -20°C. The flask was allowed to warm to room temperature with continued stirring under a slight argon purge. The dimethyl ether evaporated during this process and passed through the traps. The product, diluted in dichloromethane, hexanes, and benzene (formed from benzvalene thermal decomposition), was carried in the gas stream and collected in the traps during this process. The combined samples of product solution obtained are degassed by three freeze-pump-thaw cycles and stored over 4 Å molecular sieves at -50°C.  $^1\text{H}$  NMR analysis of the 17.9 grams of pale yellow liquid obtained indicated 4.83 grams (18% yield) of benzvalene were present.

**Polybenzvalene (PBV) Synthesis.** Toluene,  $d_6$ -benzene, and xylenes were used as solvents in different polymerizations. A typical polymerization procedure is given below.

The tungsten catalyst 7 (0.050 g, 0.060 mmol, 1.0 equiv) was dissolved in 5.4 mL of toluene in a drybox and transferred to a glass tube equipped with a stir bar and Teflon valve. The tube was attached to a high vacuum line and the stirred contents cooled to 0°C. To this were added 0.60 mL of a 0.5 M solution of benzvalene (0.235 g, 3.0 mmol, 50 equiv) in hexanes, dichloromethane, and benzene by syringe. The resulting mixture was allowed to stir at 0°C for

10 minutes and then allowed to warm to room temperature. The mixture became progressively darker.  $^1\text{H}$  NMR analysis of a sample of the mixture after 0.5 hours at room temperature showed complete consumption of the benzvalene. To quench the catalyst, 0.1 mL of dry, deoxygenated acetone (0.075 g, 1.3 mmol, 13 equiv) were added by syringe and the resulting mixture allowed to stir for 0.25 hrs.

In stabilization studies, the solution of PBV was used directly without isolation. PBV could be isolated from the solution by precipitation into methanol, but was insoluble in all organic solvents once isolated. DSC analysis (with unsealed aluminum pans) of PBV obtained in this manner gave a  $T_{\max}$  of 150°C for the first exotherm. In later DSC analysis with sealed aluminum pans, the value of  $T_{\max}$  for the first exotherm dropped to 137°C.

**Attempted PBV Hydrogenation With *p*-Tosylhydrazine .** A sample of 0.235 g of PBV in 6.0 mL of xylenes was prepared as above. The mixture was added to a solution of *p*-tosylhydrazine (3.3 g, 17.7 mmol, 5.9 equiv/monomer unit) in 4.0 mL of xylenes. The mixture was heated to 110°C. After 10 minutes a large quantity of polymer precipitated. The polymer was collected, washed with toluene, and dried overnight under high vacuum to give 0.242 g of "hydrogenated" PBV. DSC analysis (with unsealed aluminum pans) gave a  $T_{\max}$  of 142°C for the first exotherm.

**Attempted PBV Hydrogenation With Hydrazine Hydrate/ $\text{K}_3\text{Fe}(\text{CN})_6$  .** A sample of 0.235 g of PBV in 6.0 mL of toluene was prepared as above. The mixture was added to a solution of 10 mL of THF, hydrazine hydrate (2.6 g, 44.6 mmol of hydrazine, 14.8 equiv/monomer unit), 2.6 mL of ethanolamine, and 10 mL of 2-methoxyethanol. A small amount of polymer precipitated upon mixing. Under argon a solution of  $\text{K}_3\text{Fe}(\text{CN})_6$  (5.74 g, 4 mmol, 5.78 equiv/monomer unit) in 12 mL of water was added dropwise in 20 minutes. The resulting mixture was diluted with chloroform, the water layer separated, and the chloroform layer reduced in volume to 10 mL. The resulting chloroform solution was added dropwise to methanol to precipitate the polymer. The polymer was collected, washed with methanol, and dried overnight under high vacuum to give 0.060 g of "hydrogenated" PBV. DSC analysis (with unsealed aluminum pans) gave a  $T_{\max}$  of 136°C for the first exotherm.

**Attempted PBV Hydrogenation With  $\text{Rh}(\text{PPh}_3)_3\text{Cl}/\text{Hydrogen}$  .** A sample of 0.235 g of PBV in 6.0 mL of toluene was prepared as above. The polymerization mixture was added by cannula to a tube containing  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  (0.0028 g, 0.0030 mmol) and the tube briefly evacuated and then flushed with hydrogen. A hydrogen reservoir consisting of a 500 mL flask was connected to the tube and the contents of the tube stirred vigorously for 3.0 hrs. The loss of pressure of the system was minimal and only 5-10% of the expected hydrogen uptake was observed. The polymer was collected as before to give 0.200 g of "hydrogenated" PBV. DSC analysis (with unsealed aluminum pans) gave a  $T_{\max}$  of 159°C for the first exotherm.

**Attempted PBV Stabilization By the Addition of Radical Traps .** Samples of PBV in toluene were generated as above. The desired amount of radical trap (either BHT or AO 2246) was added to the solution and the "stabilized" polymer isolated by evaporation of the solvent. DSC data for the samples obtained are given in Tables 3 and 4 in the Results and Discussion Section of this report.

**Improved Synthesis of Homobenzvalene (4).** A series of reactions were run on a 50 mg scale of the starting material, 7-chloronorbornadiene (8), with the reducing agent  $\text{NaBH}_4$ . The mixtures obtained were analyzed by capillary GC, using a methylsilicone column, to determine the percent yields of the compounds obtained. The details of the experiments are given in Table 8.

**Table 8.** Experiments to Improve the Synthesis of Homobenzvalene (4)

solvent (mL)	base	NaBH <sub>4</sub> (mg)	time (h)	% 4	% 8	% 9
MeOH (1.5)	NaOH	40	1	63	19	6
MeOH (1.5)	NaOH	40	3	63	19	6
MeOH (1.5)	NaOH	40	20	63	19	6
MeOD (1.5)	NaOH	40	3	80	-	5
MeOH (1.5)	NaOH	40	18	78	-	5
MeOH - dry (1.7)	NaOH	40	18	41	30	2
MeOH - dry (1.5)	NaOMe	70	3	18	-	-
MeOH/H <sub>2</sub> O-1:1 (2)	NaOH	100	4	28	-	2
THF - dry (2)	—	100	3	-	100	-
THF/H <sub>2</sub> O-1:1 (2)	NaOH	40	3	32	23	8
Ph/H <sub>2</sub> O -1:1 (2.4)*	NaOH	80	18	58	5	20

\* Employed 80 mg of benzyltrimethylammonium chloride as a phase transfer catalyst.

**Synthesis of a Toluene Solution of 4.** To a 250 mL round bottom flask were added benzyltrimethylammonium chloride (4.06 g, 21.8 mmol, 1.1 equiv), NaOH (0.80 g, 20 mmol, 1.0 equiv), NaBH<sub>4</sub> (4.06 g, 108 mmol, 5.4 equiv). The flask was purged with argon and 40 mL of deoxygenated water added by syringe. The mixture was stirred at room temperature to dissolve all of the solids. To this mixture were added 40 mL of deoxygenated toluene and then 7-chloronorbornadiene (2.54 g, 20 mmol, 1.0 equiv), both by syringe. The resulting mixture was stirred overnight at room temperature. <sup>1</sup>H NMR analysis of a sample of the mixture indicated no starting material was left. The organic layer was separated, dried (Na<sub>2</sub>SO<sub>4</sub>), and stored over CaH<sub>2</sub> over the weekend, after degassing by several freeze-pump-thaw cycles. The mixture was then vacuum-transferred to a Schlenk tube and stored at 0°C. <sup>1</sup>H NMR analysis of the mixture indicated concentrations of 0.29 M for the product 4 and 0.081 M for the side product norbornadiene (9).

**Polyhomobenzvalene (PHBV) Synthesis With the Catalyst 10.** The catalyst 10 (0.0364 g, 0.041 mmol, 1.0 equiv) was partially dissolved in 2.9 mL of toluene and transferred to a glass tube with a Teflon valve. To the stirred dark green mixture were added, by syringe, 7.0 mL of a solution of 4 (0.29 M, 0.187 g, 2.03 mmol, 50 equiv) in toluene (also containing 9 (0.081 M, 0.052 g, 0.567 mmol, 14 equiv)). The mixture turned light brown after several minutes. <sup>1</sup>H NMR analysis of samples withdrawn during the polymerization indicated 4 was consumed while 9 remained and after 1.5 hours all of the monomer was consumed. To quench the catalyst, 2-chloroethylvinyl ether (0.0524 g, 0.49 mmol, 12.0 equiv) was added and the mixture stirred for 0.5 hours. The polymer was obtained by precipitation into methanol and dried overnight to give 0.177 g of PHBV (95% yield based on 4). The sample was soluble in dichloromethane, benzene, and THF. GPC analysis gave M<sub>n</sub> = 5,400 and M<sub>w</sub> = 20,400. The polymerization was repeated with 99 equivalents of 4 to give a sample of PHBV which was not very soluble in THF and precluded GPC analysis. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the PHBV samples obtained are presented in Figures 1 and 2 in the Results and Discussion Section of this report.

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**Preparation of Hydroxytelechelic Poly(butadiene) via Ring-Opening Metathesis Polymerization Employing a Well-Defined Metathesis Catalyst<sup>†</sup>**

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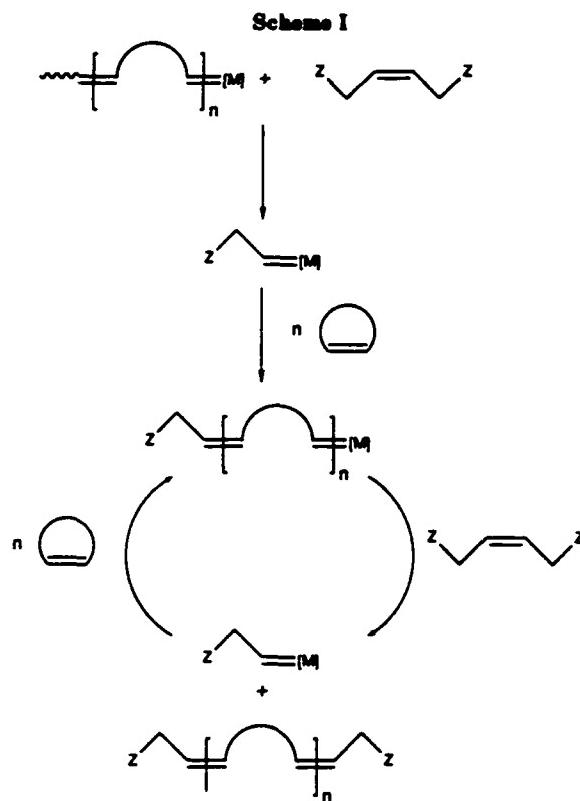
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Telechelic polymers, macromolecules with one or more reactive end-groups, are useful materials for chain extension processes, block copolymer synthesis, reaction injection molding, and network formation.<sup>1,2</sup> For most applications a functionality (number of functional groups per chain) of 2 or greater is required. In particular, commercially produced hydroxytelechelic poly(butadiene) (HTPBD) has found a variety of industrial applications.<sup>3–6</sup> Commercially available HTPBD obtained by the radical polymerization of 1,3-butadiene in the presence of hydrogen peroxide is a mixture of 1,4 and 1,2 repeat units containing at least three types of hydroxy end-groups.<sup>6–9</sup> Although the functionality of HTPBD obtained from this radical polymerization is typically greater than 2,<sup>7,10</sup> termination by disproportionation can lead to monofunctional polymers which are detrimental to the production of high molecular weight polymers in a subsequent step-growth polymerization. As with most radical polymerizations, the ease of HTPBD preparation by this method is balanced by the lack of regiospecificity and end-group specificity. The ability to systematically tailor the structure of HTPBD (both the regiochemistry and functionality) would allow a fundamental understanding of structure–property relationships in the polymer and derived copolymers. Living anionic polymerization techniques offer a potential solution, and progress has been made in this area.<sup>1,2</sup> In this paper we show that ring-opening metathesis polymerization (ROMP)<sup>11</sup> using a discrete metal alkylidene catalyst offers another alternative polymerization technique that is applicable to the synthesis of well-defined HTPBD.

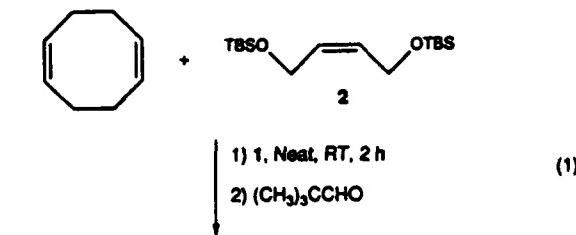
Acyclic olefins act as chain-transfer agents to regulate the molecular weight of polymers produced by ROMP.<sup>11</sup> When  $\alpha,\omega$ -difunctional olefins are employed as chain-transfer agents, difunctional telechelic polymers can be synthesized.<sup>12–15</sup> However, ill-defined classical metathesis catalysts have been employed in all cases reported to date. It is not possible either to modulate the activity of the catalyst systematically, to define the structure of the initiating alkylidene, or to control the mode of termination of these multicomponent catalysts. In addition, the Lewis acid cocatalysts typically found in these systems (e.g., AlR<sub>3</sub>, SnR<sub>4</sub>, or AlClR<sub>2</sub>) can react with functional groups of the chain-transfer agent or with the monomer itself,<sup>20</sup> leading to unwanted byproducts and catalyst deactivation. These problems can potentially be circumvented by the use of well-defined, Lewis-acid-free metal alkylidene complexes whose structure and activity can be easily modified.<sup>21–24</sup> Furthermore, these catalysts can produce living polymer chains where there is no termination of the active catalyst center in the absence of an end-capping reagent. In the chain-transfer reaction with a symmetric  $\alpha,\omega$ -difunctional olefin, the propagating alkylidene is terminated with a



functional group, and the new functionally substituted alkylidene reacts with a monomer to initiate a new chain. This process preserves the number of active catalyst centers and leads to symmetric telechelic polymers with a functionality that approaches 2.0 (Scheme I). The only polymer end-groups that do not contain residues from the chain-transfer agent are those from the initiating alkylidene and the end-capping reagent. In principle, these end-groups could be chosen to match the end-group from the chain-transfer agent. The following data are results on the preparation of HTPBD using a protected allylic diol as the chain-transfer reagent and a single-component metathesis catalyst with a well-defined initiating alkylidene.

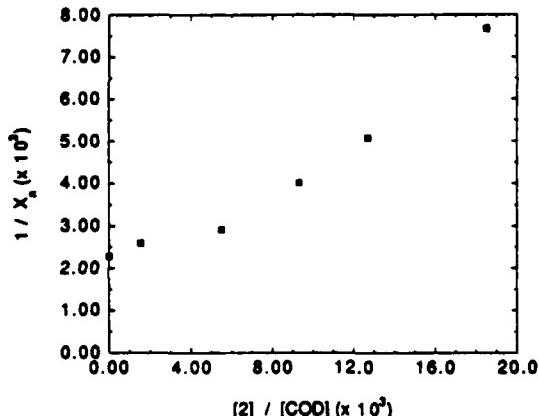
The ROMP of 1,5-cyclooctadiene (COD) leads to a polymer having a repeat unit that is identical to that of 1,4-poly(butadiene). The catalyst chosen for this study was W(CHAr)(NPh){OCCH<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(THF) (Ar = *o*-methoxyphenyl) (1), due to its ease of synthesis and high metathesis activity.<sup>22,23</sup> The chain-transfer agent was obtained by the protection of *cis*-1,4-butenediol as the bis(*tert*-butyldimethylsilyl) (TBS) ether (2).<sup>25</sup> In a typical experiment, COD and 2 were mixed in a vial under an inert atmosphere and transferred by syringe into a separate vial that contained 1 (dissolved in a minimum amount of benzene). The mole ratio of 2 to COD ranged from  $1.5 \times 10^{-3}$  to  $1.9 \times 10^{-2}$ , and the mole ratio of COD to 1 was kept constant at approximately 700. All reactions were run at room temperature for 2 h and terminated by the addition of excess pivalaldehyde (eq 1). The reaction mixtures were then dissolved in benzene and precipitated into methanol. Molecular weights of the polymers were determined by GPC in methylene chloride (referenced to polystyrene standards), and these results are shown in Table I. The molecular weights of the telechelic poly(butadiene)s decreased with increasing concentration of the chain-

\* Contribution No. 8721.



**Table I**  
Molecular Weight and Yield Data for Poly(butadiene) Telechelomers

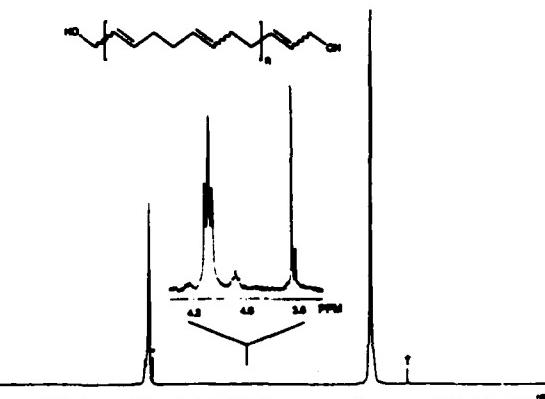
run	$([2]/[\text{COD}]) \times 10^3$	$[\text{COD}]/[1]$	$M_n \times 10^{-3}$	PDI	yield (%)
1	0	712	47.4	2.1	92
2	1.53	710	41.7	2.0	90
3	5.49	713	37.1	2.0	71
4	9.31	708	26.9	2.1	62
5	12.7	701	21.3	2.1	51
6	18.5	713	14.1	3.0	40



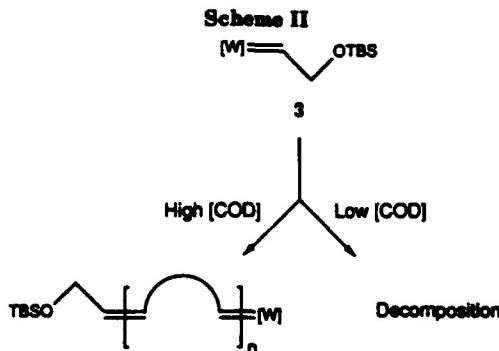
**Figure 1.** Effect of  $[2]/[\text{COD}]$  on the number-average degree of polymerization.

transfer agent. The relationship between the number-average degree of polymerization and the mole ratio of 2 to COD is shown in Figure 1.

To remove the TBS end-groups from the polymer, a THF solution of a low molecular weight TBS end-capped polymer was reacted with excess tetra-*n*-butylammonium fluoride at room temperature for 12 h. The polymer was precipitated into methanol, redissolved in benzene, and filtered twice through silica gel. The <sup>1</sup>H NMR spectrum of the purified HTPBD polymer is shown in Figure 2. Only signals from the polymer backbone and end-groups are present. The pseudotriplets at 4.14 and 4.04 ppm are assigned to the methylene protons adjacent to the oxygen (both cis and trans isomers) of the end-group. Addition of trifluoroacetic anhydride results in the downfield shift of these signals by 0.75 ppm and collapse of the pseudotriplets into doublets. End-groups from the initiating alkylidene are identified by the presence of singlets at 3.81 and 3.83 ppm. These signals were assigned to the aromatic methoxy group from the initiating alkylidene (both cis and trans isomers) and are seen in the spectra of both the protected and deprotected polymers.<sup>27</sup> The end groups from the end-capping reagent, pivalaldehyde, are not observed. Hydroxyl functionalities of 1.7–1.9 were calculated for the low molecular weight polymers.<sup>28</sup>



**Figure 2.** 400-MHz <sup>1</sup>H NMR spectrum of HTPBD in  $\text{CDCl}_3$ : (\*) solvent; (†)  $\text{H}_2\text{O}$  impurity.



The presence of end-group fragments only from the initiating alkylidene and the chain-transfer agent (2) but not from the end-capping reagent indicates that the catalyst decomposes during the course of the reaction. This likely results from the instability of the alkylidene moiety, 3, generated from the reaction of the propagating alkylidene with 2 (Scheme II). It is speculated that in the presence of high COD concentrations this alkylidene will reinitiate the polymerization, but as the concentration of COD decreases during the polymerization an alternative decomposition pathway involving the  $\beta$  oxygen becomes competitive. Consistent with this observation is the decrease in the yield of polymerization with increasing concentration of 2 (Table I) and the insensitivity of the yield to increased reaction time. Also, this hypothesis is consistent with the inability of 1 to effect the isomerization of 2 from cis to trans and with the decomposition of 1 in the presence of 2. The instability of  $\beta$ -oxygen-substituted alkylidenes is not surprising since the metathesis of allylic ethers has generally met with little success.<sup>29</sup> To alleviate this problem, the homoallylic derivative of 2 (1,6-bis(*tert*-butyldimethylsilyloxy)-cis-3-hexene) was synthesized. In preliminary experiments it was found to be an effective chain-transfer agent, and near quantitative yields of telechelic polymer were obtained. In addition, the cis-trans isomerization of this extended chain-transfer agent was effected by 1.

In conclusion, the use of a well-defined metathesis catalyst for the preparation of HTPBD has been demonstrated. The HTPBD obtained has entirely 1,4 repeat units and only one type of hydroxyl end-group. Also, the functionality of the HTPBD is close to 2.0. This system demonstrates the utility of this approach, and more efficient chain-transfer agents that will lead to stable alkylidenes, increase polymer yields, and provide other functionalities are being investigated.

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# The ROMP of COD by a Well-Defined Metathesis Catalyst in the Presence of a Difunctional Chain Transfer Agent: The Preparation of Hydroxy-Telechelic 1,4-Poly(butadiene)

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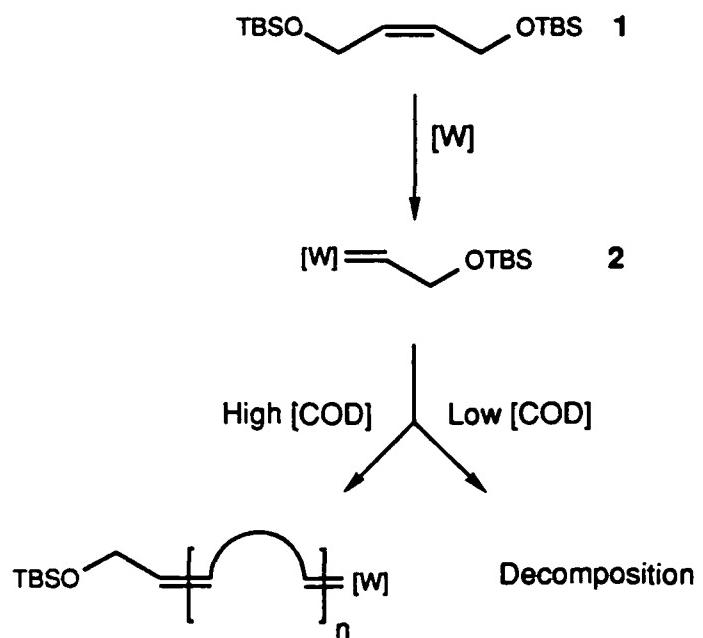
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## Introduction

The utility of well-defined metathesis catalysts has been demonstrated by the Ring-Opening Metathesis Polymerization (ROMP) of a variety of cyclic olefins.<sup>1,2</sup> Norbornene and functionalized norbornenes have received the most attention due to their high reactivity and ease of synthesis. The combination of highly reactive norbornene with the advent of the new well-defined metathesis catalysts has led to a number living polymerization systems in which molecular weight, stereochemistry, and end-groups can be easily defined. Recent efforts in our laboratories have exploited the advantages of well-defined metathesis catalysts in the polymerization of less strained cyclic olefins.<sup>3,4</sup> Study of chain transfer processes in the ROMP of cyclooctadiene (COD) is the focus of this work.

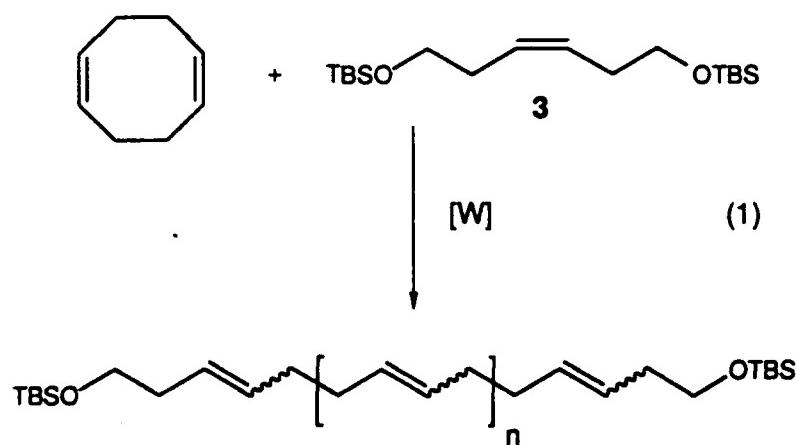
## Results and Discussion

The ROMP of COD gives a polymer that is identical in structure to poly 1,4-(butadiene). In a previous publication<sup>3</sup> we described the preparation of hydroxy-telechelic poly 1,4-(butadiene) (HTPB) through the use of a chain transfer agent (**1**) in the polymerization of COD. However, at high [1] / [COD] ratios the yield of polymer decreased markedly (from 92% to 42%). It was speculated that the metal alkylidene (**2**) formed from the chain transfer reaction decomposed at low COD concentrations due to presence of a  $\beta$  oxygen (Figure 1).



**Figure 1.** Fate of metal alkylidene fragment (**2**) in the preparation of HTPB by the ROMP of COD in the presence of **1**.

To alleviate this problem, the two carbon homologue of **1** (**3**) was synthesized and used as a chain transfer agent in the polymerization of COD (eq 1). The results of this polymerization are shown in Table I.

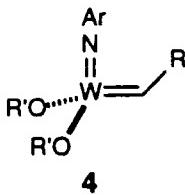


**Table I**  
**Polymerization of COD in the presence of 3**

Run	[3] / [COD]	M <sub>n</sub> (VPO)	% Yield
1	0.011	7990	94
2	0.027	4210	96
3	0.045	3490	94
4	0.093	2310	83

The yields of polymer isolated are considerably higher when **3** is used as the chain transfer agent instead of **2**. However, at high [3] / [COD] ratios a slight decrease in yield was observed (runs 3 and 4). It was determined that there was no unreacted monomer in run 4, but there was unreacted **3**. The catalyst used in all of the above

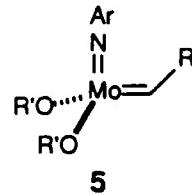
chain transfer reactions was  $\text{W}(\text{CHAr})(\text{NPh})[\text{OCCH}_3(\text{CF}_3)_2]_2$  (THF) ( $\text{Ar} = o$ -methoxy-phenyl) (4).<sup>5</sup> Again, the catalyst seems to decompose before the reaction with both the COD and 3 is complete. This was surprising since 4 will effect the cis-trans isomerization of 3 thus indicating its stability toward 3.<sup>6</sup> A more robust molybdenum catalyst (5)<sup>7</sup> was chosen in order to prevent premature decomposition.



$\text{Ar} = \text{phenyl}$

$\text{R}' = \text{C}(\text{CF}_3)_2\text{CH}_3$

$\text{R} = o\text{-methoxyphenyl}$



$\text{Ar} = 2,6\text{ diisopropylphenyl}$

$\text{R}' = \text{C}(\text{CF}_3)_2\text{CH}_3$

$\text{R} = \text{C}(\text{CH}_3)_2\text{Ph}$

When the reaction identical to run 4 was repeated with 5 as the catalyst no monomer and less than 5% (by GC) of 3 remained after 30 min at RT. In addition, 5, remains active well after the polymerization is complete as seen by the build up of cyclic oligomers at longer reaction times.

The number average functionality ( $F_n$ ) of these oligomers has been determined using the number average molecular weight ( $M_n$ ) from VPO measurements and  $^1\text{H}$  NMR integration. Under ideal circumstances,  $F_n$ 's of greater than 1.9 have been calculated. The theoretical value for  $F_n$  in this type of chain transfer system can be determined by equation 2.

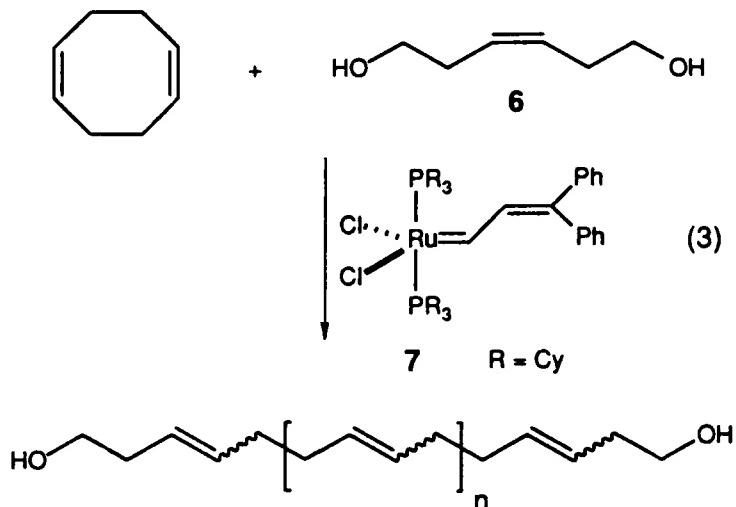
$$F_n = \frac{\# \text{ functional groups}}{\# \text{ of chains}} \quad (2)$$

$$F_n = \frac{2 \text{ [chain transfer agent]}}{\text{[chain transfer agent]} + \text{[catalyst]}}$$

When using a difunctional chain transfer agent, each chain transfer molecule is responsible for two functional groups. The total number of chains is equal to the number of chains initiated by the catalyst (i.e.  $[\text{catalyst}]_0$  at 100% initiator efficiency) plus the number of chains initiated by the metal alkylidene formed from a chain transfer reaction (i.e.  $[\text{chain transfer agent}]_0$  at complete conversion of the chain transfer agent). This equation requires a  $[\text{chain transfer agent}] / [\text{catalyst}] > 50$  for a  $F_n > 1.96$ . Under the experimental conditions used in the above polymerizations ( $[\text{COD}] / [4] \approx 900$  and  $[3] / [4] \approx 82$  for run #4) the calculated  $F_n$  of 1.97 is in good agreement with the experimental value of 1.93.

Telechelic 1,4-poly(butadiene) with predictable molecular weight and  $F_n$ 's very close to 2.0 can be synthesized using the ROMP-chain transfer system described above. One drawback, however, to the above system is the necessity to protect the alcoholic functionality in the chain transfer agent with a protecting group that is compatible with the catalyst (4 or 5). This protecting group must be removed after the preparation of the polymer. The TBS protecting group is easily removed by  $\text{F}^-$ , yet it would be desirable to use the alcohol directly. Preliminary

experiments<sup>8</sup> have shown that this can be accomplished through the use of a well-defined ruthenium alkylidene catalyst (7)(eq. 3).



Further investigation of this "unprotected" chain transfer system, theoretical aspects of ROMP-chain transfer chemistry, and applications of the HTPB synthesized by this route are currently underway.

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